ABSTRACT

THESIS: Synthesis and Mechanistic Study of Alkoxypyridinium Salt Derivatives

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DATE: July, 2011

2-Benzyloxy-1-methylpyridinium trifluoromethanesulfonate (commonly referred to as benzyloxypyridinium triflate or Dudley's salt) is a novel protecting reagent for the conversion of an alcohol functional group into a benzyl ether. This novel protecting reagent allows for protection of an alcohols, carboxylic acids, and other nucleophiles under mild conditions. The two traditional methods of forming this benzyl ether rely on either basic (Williamson ether synthesis) or acidic (coupling via trichloroacetimidate with a strong acid) conditions which may potentially decompose sensitive substrates.

This research will investigate the mechanism by which benzyloxypyridinium triflate decomposes. Investigation of benzyloxypyridinium triflate will require two aspects, synthesis of various derivatives and a rate study. The synthesis of benzyloxypyridinium triflate derivatives (broadly named benzyloxypyridinium salts) will result in a series of new compounds, along with new synthetic routes to make them. Testing the derivatives to ensure they form the expected benzyl ether or ester then allows for investigation of the rate for each derivative as they form the benzyl ether. Among the various techniques that may be employed to study the mechanism, rate studies will be a significant portion of data used to draw a conclusion. Each derivative of the benzyloxypyridinium triflate is designed to affect the rate of decomposition thereby changing the

rate of benzyl ether formation by either promoting or impeding the formation of a carbocation. Monitoring the rate of each derivative and comparing that rate to the rate of the benzyloxy-pyridinium triflate will give insight to a mechanistic pathway, indicating whether the pathway is more unimolecular or bimolecular.

An immediate application of a known mechanism could lead to more desirable conditions for the benzyloxypyridinim triflate when forming the benzyl ether. In addition, having an understanding of the mechanism allows for the utility of arylmethylpyridinium salts to be expanded by allowing the pyridinium salt to deliver a variety of different electrophiles. The mechanism will also allow for different nucleophiles to trap the corresponding electrophile from the pyridinium salt.